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Abstract

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THE INFLUENCE OF THE COMPOSITION OF BOROALUMINOSILICATE GLASSES ON THEIR ELECTRODE AND ACID PROPERTIES*

Many investigations have shown that when sodium glasses come into contact with aqueous solutions, an ion-exchange reaction occurs:

$$\mathrm{Na}^+(\mathrm{solution}) + \mathrm{H}^+(\mathrm{glass}) = \mathrm{Na}^+(\mathrm{glass}) + \mathrm{H}^+(\mathrm{solution}). \qquad (1)$$

The equilibrium constant of this reaction (the exchange constant)

$$K = \frac{a_{\mathrm{H}} \cdot N_{\mathrm{Na}}}{a_{\mathrm{Na}} \cdot N_{\mathrm{H}}}. \qquad (2)$$

characterizes the relative affinity "for the glass" of hydrogen ions and sodium ions, and at the same time the electrode and acid properties of the glass I. In equation (2), a_{H} and a_{Na} are the activities of ions in solution, and N_{H} and N_{Na} are their concentrations in the glass phase.

From the expression for the normal chemical affinity (change in free energy) of reaction (1),

$$\Delta\Phi^0 = -RT \ln K = (\mu_{\mathrm{Na}}^{0\,\mathrm{gl}} - \mu_{\mathrm{H}}^{0\,\mathrm{gl}}) - (\mu_{\mathrm{Na}}^{0\,\mathrm{sol}} - \mu_{\mathrm{H}}^{0\,\mathrm{sol}}) \qquad (3)$$

it follows that, for different glasses in one and the same solvent, the exchange constant is determined by the difference of the normal chemical potentials of sodium and hydrogen ions in the glass phase. There is reason to believe that, in changes of this difference with the composition of the glasses, the change in the chemical potential of hydrogen ions will play the more important role. Translating this into ordinary chemical language, one may say that strengthening of the acid properties of the glass, associated with weakening of the bond strength of hydrogen ions in its structure (increase of $\mu_{\mathrm{H}}^{0\,\mathrm{gl}}$), should lead to an increase in the exchange constant K and cause the equilibrium of reaction (1) to shift to the right. As was shown earlier, precisely such an increase in the exchange constant is observed upon introducing boric anhydride and aluminum oxide into sodium silicate glasses ($^{2-4}$). Borosilicate glasses have a more extended transition region from the hydrogen to the sodium function in comparison with silicate glasses. This may be connected with the presence in borosilicates of different kinds of acid groups, differing in the bond strength of hydrogen ions (borosilicate and silicate bonds). Setting ourselves the task of systematically studying the influence of these oxides on the ion-exchange properties of glasses and establishing the chemical nature of their influence, we obtained experimental data (^{5}) that made it possible to determine the values of the exchange constant for three series of sodium-calcium borosilicate and certain aluminosilicate glasses, the compositions of which are given in Table 1.

The exchange constant was determined by a previously developed method (^{3}), by studying the dependence of the potential of electrodes made from the glasses on the pH of solutions. This dependence is expressed in general form by the equation

$$\varphi = \varphi^\circ + \vartheta \lg \left(a_{\mathrm{H}} + K(a_{\mathrm{Na}})\right), \tag{4}$$

where $\vartheta = \frac{RT}{F} \cdot 2.3$. From equation (4) it is evident that the electrode properties of a glass are also determined mainly by its exchange constant. A glass whose exchange constant has a small value, i.e., one possessing weakly acidic

Table 1

Composition of glasses I (by analysis, mol. %)

Glass No.	SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO	Glass No.	SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO
1	(72)	–	–	(22)	(6)	10	67.9	9.3	–	16.5	6.3
2	68.3	3.9	–	21.5	6.3	11	65.8	11.3	–	16.7	6.2
3	65.5	6.5	–	21.9	6.1	12	63.5	14.0	–	16.5	6.0
4	62.0	9.2	–	22.7	6.1	13al	(64)	(13)	(2)	(15)	(6)
5	60.7	10.8	–	22.5	6.0	14	62.0	16.1	–	16.3	5.6
6al	(60)	(10)	(2)	(22)	(6)	15al	(59)	(18)	(2)	(15)	(6)
7	(79)	–	–	(15)	(6)	16	71.8	10.7	–	11.7	5.8
8	(74.6)	3.7	–	15.7	6.0	17	68.3	14.7	–	11.0	6.0
9	72.6	6.3	–	14.7	6.4	18	66.2	16.3	–	11.3	6.2
						19	74.0	16.0	–	10.0	–

Notes. 1. In parentheses are given the compositions of glasses that were not analyzed; these compositions are given on the basis of the synthesis. 2. The index "al" denotes glasses containing aluminum oxide.

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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

properties, will exhibit over a wide range predominantly a hydrogen function ($\varphi_{\mathrm{H}} = \varphi^0 + \vartheta \lg a_{\mathrm{H}\cdot}$). A glass with a large numerical value of the exchange constant, i.e., one possessing strongly acidic properties, will exhibit predominantly a sodium electrode function ($\varphi_{\mathrm{Na}} = \varphi^0 + \vartheta \lg K a_{\mathrm{Na}\cdot}$). Each of the glasses investigated changed, with increasing pH of the solutions, from the hydrogen to the sodium function. This made it possible to calculate the values of the constant K by means of the formula

$$-\lg K = \frac{\varphi_{\mathrm{H}\cdot} - \varphi_{\mathrm{Na}\cdot}}{\vartheta} - \lg \frac{a_{\mathrm{H}\cdot}}{a_{\mathrm{Na}\cdot}},$$

where the quantities with the indices H· and Na· correspond to the media in which the glass possesses the hydrogen or sodium function, respectively.

For all glasses, the exchange constants K were determined. As is seen from Fig. 1, which presents the dependence found for the glass exchange constant on the content of boric anhydride in them, all experimental points lie on three curves, each of which corresponds to a constant sodium oxide content. Glass No. 19 (see Table 1), which differs from the others by the absence of calcium oxide, falls outside the curve (downward).

From Fig. 1 it is seen that the numerical value of the exchange constant of the glasses increases with increasing content of boric anhydride in them and with decreasing content of sodium oxide (and calcium oxide). As with boric anhydride, aluminum oxide also affects the constant. The dependence of the exchange constant on the composition of the glass thus has a complex character.

However, this dependence is greatly simplified if the chemical role of all the indicated oxides in the glass is taken into account. The oxides of sodium and calcium are basic components of glasses, while the oxides of silicon, boron, and aluminum are acidic. In this case silicon oxide, interacting with basic oxides, gives salts of a weak acid (simple silicates), whereas boric anhydride and aluminum oxide, interacting with silicon oxide and with basic oxides, give salts of stronger acids (boro- and aluminosilicates). It has been established that, when increasing amounts of boric anhydride are added to silicate glass, the basic oxides first form boro- and aluminosilicates, while the remainder of the basic oxides gives simple silicates. Precisely this distribution of the basic oxides, also assumed on the basis of other methods of investigation ([6,7]), is clearly illustrated

by the fact that glasses containing comparable amounts of B_2O_3 and Na_2O possess strongly acidic properties (correspondingly, comparatively large values of K). Indeed, if Na^+ ions are distributed predominantly in the borosilicate groups of the initial structure of the glass,

Fig. 1. Dependence of the exchange constant K on the boron oxide content in glass at different concentrations of Na_2O:
1 –22%, 2 –15%, 3 –10%

Fig. 2. Dependence of the ion-exchange constant K on the ratio characterizing the molar fraction of salts of strong acids in the glass

$$a = \frac{B_2O_3(\%) + Al_2O_3(\%)}{Na_2O(\%) + CaO(\%)}.$$

then the weak bond of the H^+ ions replacing the Na^+ ions that corresponds to these groups determines the strongly acidic properties of the glasses. Thus, the acidic properties of the glass should increase as the relative content of boroaluminosilicates in it increases in comparison with the content of simple silicates; at the same time, the numerical value of the exchange constant should increase, and the region in which the glass exhibits the hydrogen electrode function in alkaline media should contract.

Since the exchange constant serves as a characteristic of the acidic and electrode properties of glass, on the basis of what has been said it is natural to expect that its magnitude should be determined by the ratio of the contents in the glass of salts of strong and weak acids. A measure of this ratio may be the quantity

$$a = \frac{B_2O_3(\%) + Al_2O_3(\%)}{Na_2O(\%) + CaO(\%)}.$$

The numerator of this fraction expresses the content in the glass of alumino- and borosilicates (i.e., strong acids), while the denominator expresses the total content of simple and boroaluminosilicates (i.e., the sum of weak and strong acids). As a first approximation, it may be assumed that each of the two groups of acids considered in the glass has its own value of the exchange constant (low for weak acids and high for strong acids), while the exchange constant determined experimentally (the effective constant) is a certain average value depending on the relative content in the glass of the one and the other acids ([7], [8]).

Figure 2 presents the dependence of the negative logarithm of the exchange constant of the glass on the quantity a, which may be called the molar fraction of strong acids in the glass. It is evident from the figure that all the points lie on a smooth curve; that is, the exchange constant of glasses is indeed a single-valued function of the ratio of strong and weak acids in the glass.

It follows from the foregoing that the hydrogen function of the glass electrode should manifest itself preferentially over the sodium function in glasses containing a small amount of boric anhydride and aluminum oxide in comparison with the oxides of sodium and calcium, which is in complete agreement with

Fig. 3. Extent of the transition region from the hydrogen to the sodium function of glass as a function of the B_2O_3 content at constant Na_2O content (22%) (the dashed line marks the pH interval corresponding to the transition region). Concentration of Na_2O: 1 –22%, 2 –10%

Figure 2: Fig. 3. Extent of the transition region from the hydrogen to the sodium function of glass as a function of the B_2O_3 content at constant Na_2O content (22%) (the dashed line marks the pH interval corresponding to the transition region). Concentration of Na_2O: 1 –22%, 2 –10%

experiment. Conversely, the sodium electrode function will manifest itself preferentially over the hydrogen function in glasses rich in boric anhydride and aluminum oxide and poor in bases, which also agrees with experiment. Of the glasses we studied, glass No. 19 has the sodium electrode function to the greatest extent; in it the content of boric anhydride exceeds the content of the basic oxide (sodium oxide).

Fig. 3. Extent of the transition region from the hydrogen to the sodium function of glass as a function of the B_2O_3 content at constant Na_2O content (22%) (the dashed line marks the pH interval corresponding to the transition region). Concentration of Na_2O: 1 –22%, 2 –10%.

From what has been said above concerning the dependence of the exchange constant on the ratio between strong and weak acids, it follows that the transition region from the hydrogen to the sodium function should be most extended over the pH interval for glasses in which the contents of strong and weak acids are comparable with one another. In glasses containing almost only weak acids or almost only strong acids, the transition region should have a smaller extent. From Fig. 3 it is seen that the first additions of B_2O_3 to silicate glass (the series with 22% Na_2O) noticeably broaden the transition region, while further additions somewhat narrow it. We note that decreasing the Na_2O content to 10% (at a B_2O_3 content of 10%) leads to an even stronger narrowing of the transition region and to its shift toward lower pH values. Sodium oxide in these glasses is practically completely consumed in the formation of strongly acidic borosilicate groups.

In conclusion, it may be noted that investigation of the dependence of the potential of the glass electrode on the composition of the glass makes it possible not only to solve a number of questions in the theory of the glass electrode, but is also a new method for a deeper study of the chemistry of glass.

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